

UCRL- 92158
PREPRINT

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This paper was prepared for submittal to
Scripta Metallurgica

February 21, 1985

Lawrence
Livermore
National
Laboratory

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COMMENTS ON KINETIC MODELS FOR RECRYSTALLIZATION

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Introduction

Early mathematical studies of the kinetics of recrystallization in metals conducted independently by Johnson and Mehl (1) and Avrami (2) produced the now-familiar relation between recrystallized volume fraction, f , and time, t :

$$f = 1 - \exp[B t^n] , \quad [1]$$

where B and n are constants. This relation yields linear plots of $\log \{\ln [1/(1 - f)]\}$ against $\log t$ at constant temperature. Several reviews of recrystallization studies (3-5) have shown that Eq. [1] does adequately represent early stages of recrystallization, and this relation has been used extensively in kinetic studies. However, Eq. [1] consistently and severely overestimates f in the latter stages of recrystallization. Vandermeer and Gordon (6) recognized this deficiency and suggested that it is caused by the simultaneous occurrence of recovery reactions that retard the recrystallization reaction. In an effort to obtain better correlation with experimental data, Speich and Fisher (7) developed a relation of the form:

$$f/(1 - f) = K t^n . \quad [2]$$

K , a constant at constant temperature, can be separated into an athermal component, $\exp(K_0)$, and a thermal component, $\exp(-Q/kT)$, to yield the logarithmic relation:

$$\log [f/(1 - f)] = K_0 - Q/kT + n(\log t) . \quad [3]$$

K_0 is a constant at constant temperature; Q is an effective or apparent activation energy, as discussed by English and Backofen (8); k is the Boltzmann constant; and T is the temperature in degrees Kelvin. This relation yields a linear plot for $\log [f/(1 - f)]$ against $\log t$ at constant temperature. Speich and Fisher obtained excellent correlation with Eq. [3] and extensive recrystallization data obtained from Fe - 3-1/4% Si specimens. Recent recrystallization studies at LLNL required an evaluation of these models to select the model best suited for representation of kinetic recrystallization data, and the results of this evaluation are discussed.

Results and Discussion

We used commercially pure (99.8%) vanadium for our recrystallization study. To facilitate detection of recrystallized grains, we annealed the vanadium to produce a large grain size of about 800 μm . Specimens selected to evaluate Eqs. [1] and [2] were cold rolled to a reduction of 90% and then annealed for 10, 30, 60, and 240 minutes at 800, 900, and 1000 C. A metallographic technique was developed to selectively etch deformation structures in the specimens (9). Values of f were obtained by careful visual estimates from the etched specimens and plotted in various forms in Figs. 1-3.

Fig. 1 is a plot of $\log \{\ln [1/(1 - f)]\}$ against $\log t$ using the Johnson-Mehl-Avrami relation in Eq. [1]. Each solid line in Fig. 1 is a linear least-squares fit of a group of isothermal data. The decrease in the slopes of the lines as temperature increases is a result of using the same range of times at each temperature. This produced a limited range of f values at

each temperature, and the range of f progressively increased as the annealing temperature increased. Therefore, the decrease in the slopes of the lines demonstrates the apparent retardation of the recrystallization reaction that is characteristic of Johnson-Mehl-Avrami plots. This constitutes a serious limitation of Eq. [1] that restricts the applicability of the Johnson-Mehl-Avrami relation to only the early stages of recrystallization.

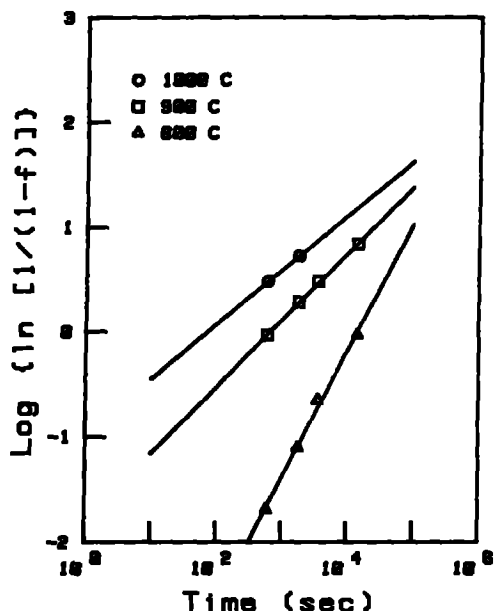


FIG. 1.

Johnson-Mehl-Avrami plot of the vanadium data; solid lines are linear least-squares fits.

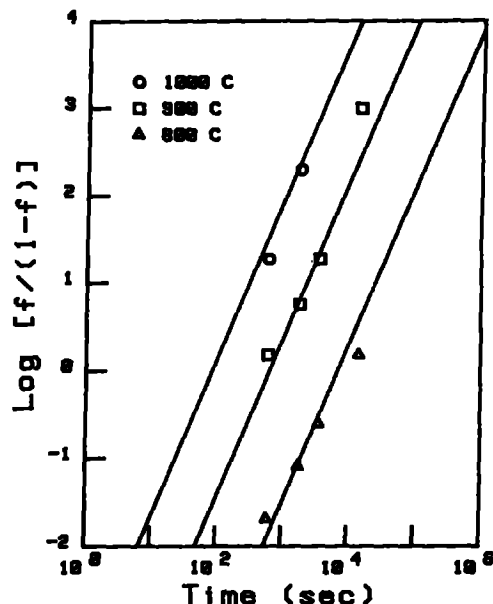


FIG. 2.

Speich-Fisher plot of the vanadium data; solid lines are from Eq. [4].

Fig. 2 is a plot of $\log [f/(1 - f)]$ against $\log t$ using the Speich-Fisher relation in Eq. [2]. A collective least-squares analysis of the vanadium data to evaluate the constants in Eq. [3] yields the relation:

$$\log [f/(1 - f)] = 34.6 - 10800/KT + 1.8(\log t) . \quad [4]$$

Because of the preliminary nature of the data, no attempt was made to conduct statistical analyses of the constants in Eq. [4]. The solid lines in Fig. 2 were calculated from Eq. [4] and show reasonable agreement with the limited experimental data. As a further demonstration of the applicability of the Speich-Fisher relation for recrystallization kinetics, Eq. [4] was used to generate a standard recrystallization plot of f against $\log t$ in Fig. 3. The solid lines in Fig. 3, which were calculated from Eq. [4], demonstrate that the Speich-Fisher relation reproduces the usual sigmoidal behavior observed in f - $\log t$ recrystallization plots. Again, the experimental vanadium data show reasonable agreement with Eq. [4] in this plot.

Standard f - $\log t$ recrystallization plots are virtually impossible to generate from the Johnson-Mehl-Avrami relation, particularly with the limited data used for this example. Furthermore, the overestimation of f for the latter stages of recrystallization by Eq. [1] produces nonsigmoidal curves when it is used to generate f - $\log t$ plots and causes a significant deviation from experimental data as f approaches 1.0. To further emphasize the nonconformance of Eq. [1] for the latter stages of recrystallization, Eq. [4] with $T = 1000$ C was used to generate points in the Johnson-Mehl-Avrami plot in Fig. 4. Points were calculated at increments of $\log t = 0.25$ and plotted as "+" symbols. The first and third points were used to plot the solid line in Fig. 4 that corresponds to the linear relation predicted by Eq. [1]. The points generated from Eq. [4] in Fig. 4 follow a pattern that is nearly identical to many previously published recrystallization plots based on Eq. [1]; the early stages of recrystallization exhibit linear behavior in accordance with Eq. [1], but the latter stages of recrystallization, as indicated by the curvature of the "+" points in Fig. 4, are significantly retarded from the rate predicted by Eq. [1]. This demonstrates the inability of Eq. [1] to predict recrystallization kinetics as f approaches 1.0. An important objective of many recrystallization studies is to

establish appropriate mechanical-working and heat-treating procedures to control grain size and obtain essentially fully recrystallized material. This requires accurate prediction of the latter stages of recrystallization and strongly favors the use of the Speich-Fisher relation in Eq. [2].

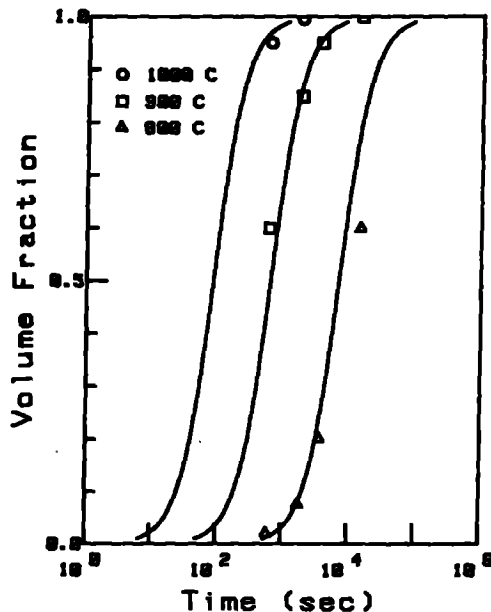


FIG. 3.

Standard recrystallization plot of vanadium data; solid curves are from Eq. [2].

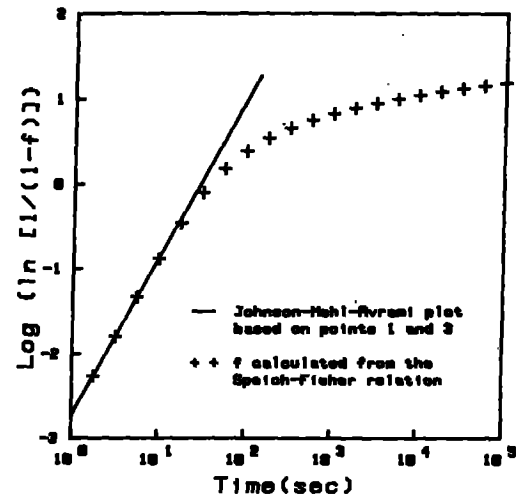


FIG. 4.

Johnson-Mehl-Avrami plot using points calculated from Eq. [4].

The Speich-Fisher relation was based on two major empirical relations. The first relation was developed from extensive experimental measurements performed on the volume fraction of recrystallized material, f , and the corresponding surface area of the interfaces between recrystallized and unrecrystallized material, A . Their experimental data corresponded to the parabolic relation:

$$A = K_a f(1 - f) , \quad [5]$$

where K_a is a constant. The second relation they used was proposed by Cahn and Hagel (10) for the rate of boundary movement during transformations. The Cahn-Hagel relation was based on a surface-averaged growth rate, G :

$$A G = df/dt. \quad [6]$$

The time dependence of G in Eq. [6] is of obvious importance. Speich and Fisher first demonstrated that if G is assumed to be constant with time, Eqs. [4] and [5] yield a relation that overestimates f for the latter stages of recrystallization to about the same extent as Eq. [1]. In fact, Johnson and Mehl (1) and Avrami (2) also assumed constant growth rates in the development of Eq. [1]. In a study of recrystallization in hot-worked Fe - 3-1/4% Si, however, English and Backofen (8) reported an experimental time-dependence of G that varied approximately inversely with time according to the relation:

$$G = K_g/t , \quad [7]$$

where K_g is essentially a constant that is independent of temperature and strain except during the initial stages of growth. Speich and Fisher derived Eq. [2] using Eqs. [5] through [7]. Both English and Backofen and Speich and Fisher presented strong arguments based on the simultaneous occurrence of recovery and recrystallization reactions to rationalize the general form of Eq. [7]. Contrary to views expressed by Gokhale, et al. (11), these arguments strongly indicate that the inability of Eq. [1] to predict the latter stages of recrystallization is a consequence of assuming a constant growth rate during recrystallization rather than a time-dependent growth rate.

The reasonably good correlation of experimental data with Eq. [2] strongly supports the use of the empirical relations in Eqs. [5] and [7]. However, Speich and Fisher emphasized that Eq. [5] was based on experimental data within the range of $f = 0.02$ to $f = 0.95$, and they clearly stated that theoretical implications of Eq. [5] outside of this range were not to be inferred. This limitation was further emphasized by Cahn (12), who demonstrated that Eq. [5] leads to implausible results when f is either small or large. His argument was based on a rigorous stereological treatment of f and A to the mean intercept length along a random line through the structure. The fact that relations identical to Eq. [2] also have been derived using constant growth rates further emphasizes the empirical nature of Eq. [2]. This was first demonstrated by Avrami (2) using the concept of extended volume to correct for impingement and assuming effectively an instantaneous and very high nucleation rate. The resulting relation was identical to Eq. [2], and Avrami also pointed out that it was identical to an empirical relation developed by Austin and Rickett (13) for isothermal transformation of austenite to bainite. More recently, Gokhale, et al. (11) used a similar approach based on extended properties along with the assumption of cylindrical growth from grain edges, and they also obtained an expression identical to Eq. [2]. This emphasizes the empirical nature of Eq. [2] but should not detract from its use in recrystallization kinetics until a better model is developed.

The fact that the Johnson-Mehl-Avrami relation provides only limited correlation with experimental data at low volume fractions, whereas the Speich-Fisher relation provides reasonably good correlation up to at least $f = 0.95$, imposes serious questions on the applicability of Eq. [1] to recrystallization kinetics. Simple numerical analysis implies that the apparent agreement of Eq. [1] with experimental data at low volume fractions is related to the insensitivity of logarithmic terms in the same range. Table 1 presents values of $\log \{\ln [1/(1 - f)]\}$ for the Johnson-Mehl-Avrami relation and $\log [f/(1 - f)]$ for the Speich-Fisher relation for select values of f . Values of $\log f$ and $\log [1/(1 - f)]$ also are included in Table 1 for purposes of comparison.

TABLE 1

Comparison of Various Logarithmic Functions of f

f	$\log \{\ln [1/(1 - f)]\}$	$\log [f/(1 - f)]$	$\log f$	$\log [1/(1 - f)]$
.000001	-5.99999978	-5.99999956	-6	0.00000043
.00001	-4.99999783	-4.99999566	-5	0.00000434
.0001	-3.99997829	-3.99995657	-4	0.00004343
.001	-2.99978276	-2.99956549	-3	0.00043451
.01	-1.99781943	-1.99563520	-2	0.00436481
.1	-0.97732211	-0.95424251	-1	0.04575749
.2	-0.65141566	-0.60205999	-0.69897000	0.09691001
.5	-0.15917454	0	-0.30103000	0.30103000
.8	0.20667423	0.60205999	-0.09691001	0.69897000
.9	0.36221569	0.95424251	-0.04575749	1
.99	0.66324568	1.99563520	-0.00436481	2
.999	0.83933694	2.99956549	-0.00043451	3
.9999	0.96427568	3.99995657	-0.00004343	4
.99999	1.06118569	4.99999566	-0.00000434	5
.999999	1.14036694	5.99999957	-0.00000043	6

These results demonstrate that the terms $\log \{\ln [1/(1 - f)]\}$, $\log [f/(1 - f)]$, and $\log f$ are nearly identical for $f < 1.0$. This occurs as f becomes small, because $(1 - f)$ approaches 1.0 and $\ln [1/(1 - f)]$ approaches f . Consequently, plots of $\log \{\ln [1/(1 - f)]\}$, $\log [f/(1 - f)]$, and $\log f$ are essentially equivalent within plotting accuracy up to about $f = 0.1$. This is the point where Eq. [2] deviates from the linear Johnson-Mehl-Avrami plot in Fig. 4, and it also corresponds to the value of f where most experimental data begin the strong deviation from linearity in Johnson-Mehl-Avrami plots. Therefore, the limited agreement of Eq. [1] with only the early stages of experimental recrystallization data appears to be more of a mathematical coincidence than agreement with theory.

Further indication of the insensitivity of the logarithmic terms is the near coincidence of $\log [f/(1 - f)]$ and $\log [1/(1 - f)]$ for $f > 0.9$. This occurs because the $(1 - f)$ term becomes dominant as f approaches 1.0. Also, these terms do not converge as f approaches 1.0, signifying

a limitation of Eq. [2]. Experience in the generation of Speich-Fisher plots indicates that the maximum value of f that should be used in Eq. [2] is about 0.99. This becomes a problem in practice only when attempts are made to plot points for $f = 1.0$ by slightly decreasing the value of f to avoid division by zero in the $\log [f/(1 - f)]$ term. However, this constitutes a limitation that should be recognized in the use of Eq. [2] and further emphasizes the empirical nature of Eq. [2].

Conclusions

The Johnson-Mehl-Avrami relation corresponds with experimental data only up to a value of about $f = 0.1$; however, this apparent agreement appears to be related more to the insensitivity of the logarithmic terms rather than agreement with theory.

Although the Speich-Fisher relation is empirical, it is strongly preferred over the Johnson-Mehl-Avrami relation for mathematical treatments of recrystallization kinetics and should be useful until a more rigorous theoretical treatment becomes available.

Acknowledgements

This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract #W-7405-ENG-48. The author gratefully acknowledges the efforts of E. L. Raymond in preparing specimens and conducting heat treatments, P. K. Ambalal in performing metallography, J. M. Bruner for editorial assistance, and W. L. Barmore, who extended his cooperation and camaraderie in the use of the Hewlett-Packard 9845B computer and plotting system on which this work was performed.

References

1. W. A. Johnson and R. F. Mehl, *Trans. AIME*, **135**, 416 (1939).
2. M. Avrami, *J. Chem. Phys.*, **7**, 103 (1939); *ibid* **8**, 212 (1940); *ibid* **9**, 212 (1941).
3. J. E. Burke and D. Turnbull, *Progress in Metal Physics*, **3**, 220 (1952).
4. R. W. Cahn, in *Physical Metallurgy*, ed. R. W. Cahn, p. 925, North-Holland, Amsterdam (1965).
5. H. Hu, in *Metallurgical Treatises*, ed. J. K. Tien and J. F. Elliott, The Met. Soc. of AIME, p. 385, Warrendale, Pennsylvania (1981).
6. R. A. Vandermeer and P. Gordon, in *Recovery and Recrystallization of Metals*, ed. L. Himmel, Interscience, **211**, New York (1963).
7. G. R. Speich and R. M. Fisher, in *Recrystallization, Grain Growth and Textures*, ed. H. Margolin, ASM, **563**, Metals Park, Ohio (1966).
8. A. T. English and W. A. Backofen, *Trans. Met. Soc. AIME*, **230**, 396 (1964).
9. P. K. Ambalal and C. W. Price, in *Microstructural Science*, Vol. **13**, Elsevier, New York, to be published.
10. J. W. Cahn and W. Hagel, in *Decomposition of Austenite by Diffusional Processes*, ed. V. F. Zackay and H. I. Aaronson, Interscience, **131**, New York (1960).
11. A. M. Gokhale, C. V. Iswaran, and R. T. DeHoff, *Met. Trans. A*, **11A**, 1377 (1980).
12. J. W. Cahn, *Trans. TMS-AIME*, **239**, 610 (1967).
13. J. B. Austin and R. L. Rickett, *Metals Technology*, T. P., No. 964 (September 1938).